

PATENT SPECIFICATION

(11) 1 284 680

1 284 680

NO DRAWINGS

- (21) Application No. 59478/70 (22) Filed 15 Dec. 1970
 (61) Patent of Addition to No. 1 233 128 dated 7 Oct. 1969
 (31) Convention Application No. P 19 65 018.1
 (32) Filed 27 Dec. 1969 in
 (33) Germany (DT)
 (45) Complete Specification published 9 Aug. 1972
 (51) International Classification C08B 19/04; C11D 7/04, 7/40; C23G 1/02
 (52) Index at acceptance
 C3U 2A1 2AX 4A3A
 C1C 220 252 30X 405
 C5D 6A4A 6A5B 6A5C 6A5D1 6A5E 6B10C 6C8
 C7E 3B
 (72) Inventors GÜNTHER SCHULZ, FRIEDRICH KRÜGER and LIESELOTTE BAUER



(54) METHOD OF PREVENTING OR INHIBITING SCALE DEPOSITION IN AQUEOUS SYSTEMS

(71) We, JOH. A. BENCKISER GMBH, CHEMISCHE FABRIK, of Jägerstrasse 30, Ludwigshafen/Rhein, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to a method for preventing or inhibiting scale deposition in aqueous systems. More particularly, the present invention is concerned with an improvement in or modification of the invention which forms the subject matter of our co-pending Application No. 49271/69 (Serial No. 1,233,128).

In our co-pending Application 49271/69 (Serial No. 1,233,128), we have described and claimed a method for the prevention or inhibition of scale deposition from aqueous systems, wherein a modified starch obtained by treatment with acid or by action of an oxidising agent, in either case below the glutinisation temperature, is introduced into this system in substoichiometric amounts (i.e. inoculation or threshold amounts) in relation to the hardening agents in the water.

The acid-modified starches used in the method of our copending Application may be obtained by mixing or treating a suspension of starch with a definite quantity of an acid, such as for example, hydrochloric acid, nitric acid, or sulphuric acid, the mixture then being heated below the glutinisation temperature until the desired degree of decomposition is obtained. Subsequently, the aqueous suspension is neutralised, the starch filtered off under suction, washed and dried in air or in a drying cupboard at 40 to 45°C.

It is also disclosed, in our co-pending Application, that the use of these acid-modified starches in admixture with certain phosphonic acids gives improved effects.

It has now been found, in accordance with the present invention, that a particularly useful acid modified starch for the prevention or inhibition of scale-forming deposits is one which has been modified with an organic phosphonic acid. Accordingly, the present invention provides a method for the prevention or inhibition of scale deposition from aqueous systems, wherein a modified starch obtained by reaction of a starch with an aqueous solution of an organic phosphonic acid, especially an amino alkylene phosphonic acid, at a temperature below the glutinisation temperature of the starch, is introduced into the system in sub-stoichiometric amounts in relation to the hardness in the water.

The starch, suitably maize or potato starch, is treated with an aqueous solution of the organic phosphonic acid, suitably in a weight ratio of starch:organic phosphonic acid of from 1:1—50:1, preferably from 4:1—10:1. The resulting product is suitably used, in accordance with the invention, in amounts of up to 500 milligrams per litre of water, preferably from 10—50 mg per litre of water.

It is an especial advantage of the present invention that products having a good threshold effect may be obtained by direct treatment of the starch with an organic phosphonic acid solution without the need to first substantially decompose the starch before admixture with the phosphonic acid solution.

It is a particularly useful characteristic of the present invention that the aqueous solution of phosphonic acid with which the starch

- is modified, may be a crude aqueous solution obtained during the commercial production of the phosphonic acid, thereby obviating the need for time consuming, expensive isolation and purification of the phosphonic acid itself. In accordance with the invention, the phosphonic acid solutions are reacted with the starch until a solid mass is obtained and thus produce the products of the invention.
- Organic phosphoric acids which may be used to modify the starch include:
- Amino-tris-(methylene phosphonic acid),
 - Diethylenetriamine - penta - (methylene phosphonic acid),
 - Ethylenediamine - tetra - (methylene phosphonic acid),
 - 1,2 - propylenediamine - tetra - (methylene phosphonic acid),
 - 1,3 - propylenediamine - tetra - (methylene phosphonic acid),
 - 1,2-cyclohexanediamine - tetra - (methylene phosphonic acid),
 - 1 - aminomethyl - cyclopentylamine(2)-tetra - (methylene phosphonic acid),
 - Hydroxyethane - 1,1 - diphosphonic acid, and
 - Aminoethane - 1,1 - diphosphonic acid.
- The modified starches used in the invention, may, for example, be obtained by mixing, in a kneader, 2 parts by weight of a 50 wt. % solution of the phosphonic acid with 4 parts by weight of maize starch or 7 parts by weight of potato starch. The mixture is then kneaded to give a solid mass which mixture already has good scale-inhibiting effects. If desired, the kneaded mixture or product may be dried, for example at 45°C, to obtain a dry or powdery product.
- The inoculation effect of the modified starches of the invention and their synergistically increased activity as compared with their individual components are shown with reference to the Examples which are summarised in the following Tables.
- In order to determine the inoculation effect, a predetermined amount (mg) of the substance to be tested was added to 1 litre of water of about 15° dH (degrees of hardness) in a 1,000 ml beaker and 12 grams of caustic soda and a glass rod were added thereto. The beaker was then covered with a watch glass and allowed to stand at ambient temperature and was periodically examined to see whether crystals had deposited on the glass rod or on the wall of the beaker.

TABLE 1

Inoculation Effect of Organic Phosphoric Acids
(Component a)

Substance	Quantity	Days							
		1	2	3	4	5	6	7	8
I Diethylenetriamine-penta-(methylene phosphonic acid)	2.5 mg	0	0	-	-	-	-	-	-
II 1,3-propylenediamine-tetra-(methylene phosphonic acid)	2.5 mg	-	-	-	-	-	-	-	-
	5.0 mg	0	0	0	0	-	-	-	-
III 1,2-propylenediamine-tetra-(methylene phosphonic acid)	2.5 mg								
	5.0 mg	0	0	0	0	-	-	-	-
IV Triethylenetetramine-hexa-(methylene phosphonic acid)	2.5 mg	-	-	-	-	-	-	-	-
V 1-aminomethyl-cyclopentylamine(2)-tetra-(methylene phosphonic acid)	2.5 mg	-	-	-	-	-	-	-	-

0 = No deposit on glass rod and on beaker wall.

- = Deposit on glass rod or beaker wall.

TABLE 2
Inoculation Effect of Starch (Component b)

	Substance	Quantity	Days							
			1	2	3	4	5	6	7	8
I	Maize Starch	15 mg	-	-	-	-	-	-	-	-
		30 mg	-	-	-	-	-	-	-	-
II	Potato Starch	25 mg	-	-	-	-	-	-	-	-
		45 mg	0	-	-	-	-	-	-	-

0 = No deposit on glass rod and on beaker wall.

- = Deposit on glass rod or beaker wall.

TABLE 3

Inoculation Effect of Modified starches produced from Components

Mixture a+b	mg mixture for inoc. test	mg phosphonic acid in mixture	Days									
			2	4	6	8	10	12	14	16	18	
a _I (50%)=20g b _I =30g	10	2	0	0	0	0	0	0	-	-	-	
a _I (50%)=20g b _I =40g	15	2.5	0	0	0	0	0	0	-	-	-	
a _{II} (50%)=20g b _I =40g	30	5.0	0	0	0	0	0	0	0	0	0	
a _I (50%)=20g b _{II} =70g	22.5	2.5	0	0	0	0	0	0	0	0	0	
a _I (70%)=14.3g b _{II} =40g	13.5	2.5	0	0	0	0	0	0	0	0	0	
a _{III} (50%)=20g b _I =40g	30	5.0	0	0	0	0	0	0	-	-	-	
a _{IV} (50%)=20g b _{II} =70g	22.5	2.5	0	0	0	0	0	-	-	-	-	
a _V (50%)=20g b _{II} =70g	22.5	2.5	0	0	0	0	0	-	-	-	-	

0 = No deposit on glass rod and on beaker wall.

- = Deposit on glass rod or beaker wall.

5 The Examples referred to above, were carried out in the alkali region in order to show the advantageous stabilising effect in a medium which is used in very many cleaning processes, but there is a stabilising effect whatever the pH of the water.

10 The method of the invention is suitable for use in all systems containing water such as cooling water equipment, evaporators and the like. The modified starches used in accordance with the invention do not lose their activity even at higher temperatures.

15 One particular possible application of the modified starches in accordance with the invention is their use in alkaline cleaning solutions. Thus, the modified starches may be included in, for example, solutions to be used

in automatic bottle rinsing machines or they may be used in the cleansing of tanks or containers. Here, particularly, when rinsing with water, during which stage of the cleaning process the cleaning agents are still present and which are diluted and rinsed out with a great deal of water, precipitation and scale deposition easily occurs. This may be prevented with inoculation or threshold amounts of the products described above in the subsequent rinsing solution. If necessary, small subsequent dosing may take place in zones which are particularly liable to scale deposition.

The modified starches used in accordance with the invention may be incorporated into solid or liquid cleaners. A suitable cleaner has,

for example, the following composition:—

	Sodium silicate	35.0%
	Product of Invention	3.0%
	Soda	20.0%
5	Caustic soda	17.0%
	Wetting Agent	5.0%
	Sodium sulphate	10.0%
	Trisodium-monophosphate.	10.0%

One percent aqueous solutions of the mixture can, for example, be used for cleaning milk churns.

WHAT WE CLAIM IS:—

1. A method for the prevention or inhibition of scale deposition from aqueous systems, wherein a modified starch obtained by reaction of a starch with an aqueous solution of an organic phosphonic acid at a temperature below the gelatinisation temperature of the starch, is introduced into the system in sub-stoichiometric amounts in relation to the hardness in the water.
2. A method as claimed in claim 1 in which the organic phosphonic acid is:—
 - Amino - tris - (methylene phosphonic acid),
 - Diethylenetriamine - penta - (methylene phosphonic acid),
 - Ethylenediamine - tetra - (methylene phosphonic acid),
 - 1,2 - propylenediamine - tetra - (methylene phosphonic acid),
 - 1,3 - propylenediamine - tetra - (methylene phosphonic acid),
 - 1,2-cyclohexanediamine - tetra - (methylene phosphonic acid),
 - 1 - aminomethyl - cyclopentylamine(2)-tetra - (methylene phosphonic acid),
 - Hydroxyethane - 1,1 - diphosphonic acid, or
 - Aminoethane - 1,1 - diphosphonic acid.

3. A method as claimed in claim 1 or claim 2 in which the weight ratio of starch to modifying acid is from 1:1 to 50:1.

4. A method as claimed in claim 3, in which the weight ratio of starch to modifying acid is from 4:1 to 10:1.

5. A method as claimed in any one of the preceding claims in which the starch is potato starch.

6. A method as claimed in any one of claims 1—4 in which the starch is maize starch.

7. A method as claimed in any one of the preceding claims in which the modified starch is used in an amount of up to 500 mg. per litre of water.

8. A method as claimed in claim 7 in which the modified starch is used in an amount of from 10 to 50 mg per litre of water.

9. A method as claimed in claim 1 substantially as hereinbefore described with reference to any of the Examples.

10. A method as claimed in any one of the preceding claims in which the aqueous system is a washing solution.

11. A modified starch product obtained by reacting a starch with an aqueous solution of an organic phosphonic acid at a temperature below the gelatinization temperature of the starch.

12. A modified starch as claimed in claim 11, as defined in any one of claims 2—5.

13. A modified starch as claimed in claim 11 substantially as hereinbefore described.

14. A washing agent containing a modified starch as claimed in any one of the claims 11—13.

MARKS & CLERK,
Chartered Patent Agents,
57 & 58 Lincoln's Inn Fields,
London, WC2A 3LS,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

THIS PAGE BLANK (USPTO)